

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

## IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.

**THIS PAGE BLANK (USPTO)**

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>4</sup> :  C08J 9/28	A1	(11) International Publication Number: WO 86/ 02656  (43) International Publication Date: 9 May 1986 (09.05.86)
(21) International Application Number: PCT/US85/02078  (22) International Filing Date: 22 October 1985 (22.10.85)  (31) Priority Application Number: 664,244  (32) Priority Date: 24 October 1984 (24.10.84)  (33) Priority Country: US	GA (OAPI patent), GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, RO, SD, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent).	Published <i>With international search report.</i>
(71)(72) Applicant and Inventor: ZACHARIADES, Anagnostis, E. [GR/US]; 65 Glengarry Way, Hillsborough, CA 94010 (US).  (74) Agent: WICKERSHAM, Robert, E.; Owen, Wickersham & Erickson, 433 California Street, 11th Floor, San Francisco, CA 94104 (US).  (81) Designated States: AT (European patent), AU, BB, BE (European patent), BG, BR, CF (OAPI patent), CG (OAPI patent), CH (European patent), CM (OAPI patent), DE (European patent), DK, FI, FR (European patent),		
(54) Title: ULTRA-HIGH-MOLECULAR-WEIGHT POLYETHYLENE PRODUCTS INCLUDING VASCULAR PROSTHESIS DEVICES AND METHODS RELATING THERETO AND EMPLOYING PSEUDO-GEL STATES		
(57) Abstract		A pseudo-gel comprising a suitable solvent in an amount of 1 to 10 percent by weight and an ultra-high-molecular-weight polyethylene in an amount of 99 to 90 percent by weight, said polyethylene being a semicrystalline network with adjustable crystalline morphology comprising randomly dispersed and oriented chain-folded single crystals, stacks of single crystals, spherulite crystals, and extended-chain shish-kebab-type of fibrils with lengths up to a few millimeters and widths up to 20 µm. Also, the semicrystalline ultra-high molecular-weight polyethylene obtained by removal of said solvent from the pseudo-gel. Further, the method for making the pseudo-gel and the ultra-high-molecular-weight polyethylene product.

***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT Austria	GA Gabon	MR Mauritania
AU Australia	GB United Kingdom	MW Malawi
BB Barbados	HU Hungary	NL Netherlands
BE Belgium	IT Italy	NO Norway
BG Bulgaria	JP Japan	RO Romania
BR Brazil	KP Democratic People's Republic of Korea	SD Sudan
CF Central African Republic	KR Republic of Korea	SE Sweden
CG Congo	LI Liechtenstein	SN Senegal
CH Switzerland	LK Sri Lanka	SU Soviet Union
CM Cameroon	LU Luxembourg	TD Chad
DE Germany, Federal Republic of	MC Monaco	TG Togo
DK Denmark	MG Madagascar	US United States of America
FI Finland	ML Mali	
FR France		

- 1 -

1           ULTRA-HIGH-MOLECULAR-WEIGHT POLYETHYLENE  
2           PRODUCTS INCLUDING VASCULAR PROSTHESIS DEVICES AND  
3           METHODS RELATING THERETO AND EMPLOYING PSEUDO-GEL STATES

4  
5           S P E C I F I C A T I O N  
6

7           This invention relates to a novel ultra-high-  
8 molecular-weight polyethylene product, useful for vascular  
9 prosthesis devices and for both industrial and biomedical  
10 uses calling for high-impact, low-friction, high wear-  
11 resistance, high-porosity, and softness or for one or more  
12 of these qualities. The invention also relates to such  
13 devices. It further relates to a novel method for processing  
14 solution-grown ultra-high molecular weight polyethylene  
15 crystalline morphologies which may form pseudo-gel states  
16 when the polymer is dissolved in a suitable volatile or  
17 non-volatile solvent at an elevated temperature and the  
18 solution is cooled to or below the temperature at which the  
19 polymer crystals are grown. Additionally it relates to  
20 methods involving further processing of the pseudo-gel  
21 states and their products after solvent extraction into  
22 profiles and shapes with physical and mechanical properties  
23 that may be tailored to specific biomedical (e.g., vascular  
24 and orthopedic prosthesis and sutures) and industrial  
25 applications.

26  
27 Background of the Invention

28           Qualities such as softness, porosity, and bio-  
29 compatibility have long been sought in the field of vascular  
30 prosthesis.

31           The development of vascular prostheses has been a  
32 subject of extensive work over the last 25 years. Most  
33 synthetic vascular prostheses have been products of the  
34 application of textile technology in this field and have  
35 been woven or knitted tubular structures designed to  
36 resemble the softness and flexibility of the natural blood

37  
38

- 2 -

1 vessels. The two major synthetic polymers used as vascular  
2 prostheses have been Dacron polyester and polytetra-  
3 fluoroethylene (PTFE).

4 These woven or knitted tubular structures are porous  
5 and have been produced with smooth or velour surfaces. The  
6 porosity, which has been claimed to play a determinant role  
7 for the healing process of the arterial prostheses, can be  
8 controlled to some extent by adjusting the thread size, or  
9 the interstices size, and by the texturization or knit  
10 pattern of the synthetic fabric. High degrees of porosity  
11 may lead to excessive blood loss after implantation; the  
12 velour has been claimed to have the advantage that it fills  
13 the interstices of the underlying fabric, thus reducing  
14 implant bleeding without reducing the porosity of the  
15 implant.

16 The DeBakey Ultra-light-weight Knitted Prosthesis  
17 (USCI, Inc.), the Cooley Graft and the Wesolowski Weavenit  
18 (Meadox, Inc.) and the Microknit (Golaski Lab, Inc.) are  
19 "smooth wall" commercial Dacron arterial prostheses of  
20 different geometric and compositional configurations; the  
21 Sauvage Filamentous Velour Prosthesis (USCI, Inc.) is an  
22 example of a velour Dacron vascular prosthesis material.

23 Woven PTFE prostheses have low porosity and have not  
24 been used as much as the Dacron prostheses. Also, it has  
25 been suggested that their use should be temporary, their  
26 permanent use being "dangerous". More recently, "expanded"  
27 PTFE, called "Gore-tex" (W. L. Gore & Assoc., Inc.) has  
28 become available. "Gore-tex" is a network of small nodules  
29 interconnected by thin fibrils and with an adjustable  
30 porosity from 0 to 96%, and it has been used with generally  
31 encouraging results. Studies with smooth vascular prostheses  
32 of expanded PTFE (85% porosity) and with ultra-light weight  
33 woven PTFE showed that the patency (i.e., openness or non-  
34 occlusion) of the expanded PTFE prostheses was significantly  
35 longer (4.5 - 10 months) in comparison to the woven PTFE

36

37

38

- 3 -

1 prostheses, which occluded in 101 days. It was also  
2 demonstrated that the porosity played a critical role in the  
3 healing process.

4 A recent theoretical calculation of the porosity in  
5 woven fabrics shows that although their porosity can be  
6 designed to vary over a wide range, the existing woven  
7 vascular prostheses, e.g. Woven Cooley and Woven DeBakey  
8 prostheses have had a low degree of porosity which might not  
9 permit complete healing, particularly in small diameter,  
10 low-blood-flow locations where the 5 year patency rate is  
11 less than 30%.

12 Ultra-high-molecular-weight polyethylene (UHMWPE) is  
13 another polymer which has attracted the interest of many  
14 workers for the preparation of artificial prostheses,  
15 particularly the construction of orthopedic joint devices,  
16 because of its outstanding abrasion resistance and strength.  
17 UHMWPE, in contrast to the conventional high-density poly-  
18 ethylenes having average molecular weights up to approxi-  
19 mately 400,000, has an extremely high molecular weight,  
20 typically 2 - 8 million, and is intractable. The polymer is  
21 supplied as fine powder and is processed into various  
22 profiles using compression molding and ram extrusion  
23 processes. The intractability of the polymer can be overcome  
24 by varying the degree of material cohesion and its initial  
25 morphology, more specifically by the formation of gel states  
26 and single-crystal mat morphologies and by heating the  
27 polymer melt to high temperature ranges, under inert  
28 conditions, in which the viscosity of the melt is reduced  
29 significantly for melt processing. The preparation of UHMWPE  
30 gel states and single crystal mat morphologies have been  
31 pursued predominantly for the development of ultra-high  
32 modulus and strength fibers. Melt processing of UHMWPE at  
33 high temperatures under inert conditions has been investi-  
34 gated for the development of melt-crystallized morphologies  
35 with enhanced mechanical properties which may result from  
36 the material cohesion which is achieved by processing under  
37 such conditions.

- 4 -

1        Although the prior art covers to a large extent the  
2 preparation of superstrong UHMWPE fibrous morphologies by  
3 spinning processes which involve a gel intermediate, the  
4 focus of the works has been mainly on the development of  
5 filamentary products with high modulus and strength in one  
6 direction. Also, there has been an expressed desire that  
7 such filamentary products have reduced porosity, because  
8 porosity may have an adverse effect on the effective  
9 transmission of load within the oriented filamentary  
10 products. On the contrary, the development of products with  
11 bulk properties or enhanced isotropic mechanical properties  
12 from gel-like precursors has received no attention.  
13 Furthermore, little effort has been devoted to determining  
14 the effect of the morphology of the gel-like precursor on  
15 the physical properties and the deformability of the  
16 products form gel-like precursors. These areas fall within  
17 the scope of my invention and they have a potential impact  
18 on the production of biomedical devices such as vascular and  
19 orthopedic prostheses and sutures and also on the  
20 fabrication of profiles possessing the outstanding wear  
21 properties of UHMWPE.

22       An example of a stretched UHMWPE fiber and a process  
23 for making it is U.S. Patent No. 4,413,110. There a slurry  
24 of polymer in paraffin oil is heated to between 180° and  
25 250°C., preferably 200°-240°C. and is then cooled to a  
26 temperature between -40°C and +40°C., the paraffin oil being  
27 replaced by a more volatile solvent at a temperature below  
28 50°C. and the cooling being rapid and done in such a way as  
29 to produce a "gel fiber". This "gel fiber" is then treated  
30 to evaporate the more volatile solvent and to stretch the  
31 "xerogel" fiber, as it is called, at 120°C + 160°C.,  
32 preferably above 135°C. The porosity of the resultant fiber  
33 is stated to be "no more than about 10% (preferably no more  
34 than about 6% and more preferably no more than about 3%)".

35

36

37

38

- 5 -

## 1 Summary of the Invention

The present invention includes the formation and use  
of UHMWPE pseudo-gels.

The term gel in the prior art referred to a macroscopically coherent structure, that (1) is spatially cross-linked, (2) comprises a major amount of low molecular-weight liquid, and (3) exhibits elastic properties not unlike those of solids.

9 On the contrary, in this specification and in the  
10 claims the terms "pseudo-gel" and "gel-like" refer to a  
11 concentrated solution of organic polymer which contains an  
12 entangled three-dimensional semicrystalline network the  
13 morphology of which may vary with the conditions of  
14 preparation or crystallization, for example, when the  
15 pseudo-gel of this invention is prepared under isothermal  
16 and quiescent conditions, the crystals in the pseudo-gel  
17 have predominantly a lamellar morphology, with single  
18 crystals or spherulitic crystals. The number of single  
19 crystals decreases, and the crystalline morphology becomes  
20 more complex as the solution concentration increases. On the  
21 other hand, when the pseudo-gel of this invention is  
22 prepared under non-isothermal and quiescent conditions, a  
23 large fraction of extended chain crystals (shish-kebab  
24 crystals) are also present. However, because the molecular  
25 entanglements in this semicrystalline network are not  
26 permanent, such solutions undergo flow when a shear stress,  
27 no matter how small, is applied. Therefore, such pseudo-gels  
28 exhibit time-dependent elastic properties and are not true  
29 gels, as the term is properly used, because they do not  
30 possess an equilibrium shear modulus.

31 In contrast to the prior art, the present invention  
32 provides for the preparation of an UHMWPE crystalline  
33 morphology with isotropic mechanical properties from a  
34 pseudo-gel precursor. Different crystalline morphologies are  
35 obtainable under different processing conditions. This  
36 crystalline morphology has an enhanced porosity which cannot

- 6 -

1 be exhibited by melt-crystallized morphologies, and it is  
2 readily deformable in the solid state into products with  
3 different properties in one or more directions.

4         This invention provides a method for the preparation  
5 of UHMWPE vascular prostheses by processing the UHMWPE in  
6 the pseudo-gel state. The pseudo-gel is prepared by  
7 dissolving a suitable concentration of the polymer in a  
8 suitable solvent, preferably a non-volatile solvent, at an  
9 elevated temperature well above the temperature at which the  
10 pseudo-gel forms and then cooling to or below the  
11 temperature at which the polymer crystals grow and the  
12 pseudo-gel forms. The pseudo-gel is subsequently processed  
13 under compression or tension into products of different  
14 profiles. Extraction of the solvent from the shaped pseudo-  
15 gel products leads to semi-crystalline porous morphologies  
16 with geometrical configurations analogous to those of their  
17 pseudo-gel precursors. These morphologies may be processed  
18 further, at a temperature below or close to their melting  
19 point.

20         This invention provides also a method for the  
21 construction of vascular prostheses by (a) compressing the  
22 pseudo-gels into thin films between hot plates, e.g., at  
23 100-170°C., (b) wrapping the pseudo-gel film around a  
24 rotating mandrel into a multilayer tubular structure, and  
25 (c) extracting the non-volatile solvent from the tubular  
26 structure on the mandrel, for example extracting first with  
27 a more volatile solvent and then drying out the tubular  
28 structure by evaporating the more volatile solvent.

29         This invention also provides for the preparation of  
30 anisotropic UHMWPE morphologies with enhanced mechanical  
31 properties, obtained by solid-state deforming, i.e., at a  
32 temperature near or below the melting point of UHMWPE, the  
33 semicrystalline polymer after extraction of the solvent, by  
34 extrusion, drawing, molding, and forging techniques.

35

36

37

38

- 7 -

1        This invention also provides for the preparation of  
2 an UHMWPE semicrystalline material which has adjustable  
3 porosity from zero up to more than 90%. This material can be  
4 made with sufficient body to maintain its shape and cross-  
5 sectional area; it is uniformly expansive and readily  
6 deformable to generate products with bulk properties, in  
7 contrast to filamentary products.  
8

9 Brief Description of the Drawings

10

11        Fig. 1 is a flow sheet of a process embodying the  
12 principles of the invention.  
13

14        Fig. 2 is a flow sheet of another process embodying  
15 the principles of the invention.  
16

17        Fig. 3 is a flow sheet of a third process embodying  
18 the principles of the invention.  
19

20        Fig. 4 is an optical photomicrograph at about 100x  
21 of a UHMWPE pseudo-gel morphology prepared under non-  
22 isothermal and quiescent conditions (NIQ). The morphology  
23 was viewed with cross-polarized light.  
24

25        Fig. 5 is a reproduction of a scanning electron  
26 micrograph of a UHMWPE semicrystalline morphology obtained  
27 from the pseudo-gels after solvent extraction and drying,  
28 according to the invention, the pseudo-gel having been  
29 prepared under isothermal and non-quiescent conditions  
30 (INQ).  
31

32        Fig. 6 is a similar scanning electron micrograph  
33 reproduction of a greater enlargement of the same kind of  
34 UHMWPE semicrystalline morphology of this invention the  
35 pseudo-gel having been prepared under isothermal and non-  
36 quiescent conditions (INQ).  
37

38

- 8 -

1        Fig. 7 is an optical photomicrograph at about 100x  
2 of a UHMWPE pseudo-gel morphology obtained under isothermal  
3 and non-quiescent conditions (INQ). The morphology was  
4 viewed with cross-polarized light.  
5

6        Fig. 8 is a similar scanning electron micrograph  
7 reproduction of a semicrystalline UHMWPE morphology of the  
8 invention obtained from the pseudo-gel after solvent  
9 extracting and drying, the pseudo-gel having been prepared  
10 under isothermal and quiescent conditions (IQ).  
11

12       Fig. 9 is an optical photomicrograph at about 100x  
13 of a UHMWPE pseudo-gel morphology obtained under isothermal  
14 and quiescent conditions (IQ). The morphology was viewed  
15 with cross-polarized light.  
16

17       Fig. 10 is a graph plotting Young's modulus versus  
18 draw ratio for a UHMWPE of this invention. The solid-line  
19 curve represents observed values and the broken-line curve  
20 shows estimated maximum values for the UHMWPE of this  
21 invention.  
22

23       Fig. 11 is a similar graph for a conventional  
24 polyethylene, but not a UHMWPE.  
25

26 Description of Some Preferred Embodiments of the Invention

27       As shown in Fig. 1, an UHMWPE pseudo-gel according  
28 to this invention may be prepared from a raw UHMWPE powder  
29 by dissolving the UHMWPE in a solvent at 21, preferably a  
30 non-volatile solvent such as paraffin oil, in a temperature  
31 range from 140 - 170°C., preferably in the high end of the  
32 temperature range in order to disrupt the thermally  
33 persistent extended chain morphology of the raw UHMWPE  
34 powder and decrease the number of nucleation sites which  
35 allow for the preparation, upon cooling, of large lamellar  
36 single crystals. These are known to have a more regular  
37 chain folded crystalline morphology than melt-crystallized  
38

- 9 -

1 and solution-grown crystal morphologies obtained by rapid  
2 cooling, and therefore have fewer intercrystalline and  
3 intracrystalline tie molecules. Such tie molecules affect  
4 the deformation behavior of the semicrystalline morphologies  
5 that are obtained after extraction of the solvent from the  
6 pseudo-gel.

7 An UHMWPE used in this work was a HiFax 1900  
8 (Hercules, Inc.) with an average molecular weight of 2 - 8 x  
9  $10^6$ . The UHMWPE was added slowly to the paraffin oil (MCB  
10 Reagents, EM Science, PX 0045-3) to concentrations from 1 to  
11 8% by weight. To avoid degradation of the polymer at high  
12 temperatures, the polymer is preferably stabilized with  
13 approximately 0.5 wt. % (based on the polymer) of BHT  
14 antioxidant (butyl hydroxy toluene) and heated under inert  
15 conditions. The mixtures were stirred slowly under constant  
16 conditions at a temperature of 150°C. A solution 22 was  
17 obtained that appeared clear until it was cooled in step 23  
18 to a temperature of approximately 123°C., where it became  
19 opaque as the pseudo-gel was formed.

20 The uniformity of a so-produced UHMWPE pseudo-gel 24  
21 depends on the conditions of preparation. When the crystals  
22 are grown in the concentrated solution under non-isothermal  
23 and quiescent conditions, herein called NIQ, the UHMWPE  
24 pseudo-gel is non-uniform and is comprised of a mixture of  
25 single crystals and a fibrillar network in which the fibrils  
26 have a shish-kebab crystalline morphology; the shish kebab  
27 fibrils in the UHMWPE pseudo-gel can be up to 2 - 3 mm. long  
28 and 20  $\mu\text{m}$ . wide. This non-uniform structure is shown in Fig.  
29 4.

30 The semicrystalline morphologies in Figs. 5 and 6  
31 were obtained from the pseudo-gel shown in Fig. 7 which was  
32 prepared under isothermal and non-quiescent conditions,  
33 herein called INQ. These semicrystalline morphologies were  
34 prepared by solvent extraction of the pseudo-gel followed by  
35 drying. Fig. 5 is a scanning electron micrograph of such a  
36 semicrystalline morphology; the degree of magnification is  
37 shown by the white bar which corresponds to 0.1 mm. in the  
38

- 10 -

1 actual semicrystalline morphology. A further magnification  
2 is shown in Fig. 6, when the white bar corresponds to 10  $\mu\text{m}$ .  
3 Fig. 7 is taken from an optical photomicrograph of the  
4 pseudo-gel at about 100x and shows a typical shish-kebab  
5 fibrillar structure surrounded by randomly oriented single  
6 crystals and stacks of single crystals, as viewed with  
7 cross-polarized light.

8 Thus, UHMWPE pseudo-gels prepared under either non-  
9 isothermal or non-quiescent conditions exhibit remarkable  
10 continuity and resistance to shear deformation.

11 The pseudo-gel shown in Fig. 9 was prepared under  
12 isothermal and quiescent conditions, herein called IQ. When  
13 the pseudo-gelation process occurs under isothermal and  
14 quiescent conditions, the pseudo-gel is more uniform, has a  
15 more turbid texture, and consists mainly of stacks of single  
16 crystals and large spherulitic crystals (up to 200  $\mu\text{m}$  in  
17 diameter) with a significantly diminished fraction of shish  
18 kebab fibrils, and resistance to shear deformation. Fig. 8  
19 is a scanning electron micrograph of the semicrystalline  
20 morphology obtained by solvent extraction and drying of a  
21 pseudo-gel like that of Fig. 9.

22 The different crystalline morphologies of the UHMWPE  
23 pseudo-gels obtained under different conditions of  
24 preparation can be ascertained also by the thermal behavior  
25 of the semicrystalline UHMWPE products which are obtained by  
26 extracting, in step 25, the paraffin oil from the pseudo-gel  
27 precursor with a more volatile solvent such as hexane, and  
28 subsequently evaporating out, step 26, the volatile solvent  
29 off in a drying process, leaving a semicrystalline UHMWPE  
30 morphology 27. The results of the thermal analysis are  
31 summarized in Table I.

32

33

34

35

36

37

38

- 11 -

1

TABLE I

2

3

4

5

6

7

8

9

10

Thermal analysis data of semicrystalline  
UHMWPE morphologies from gel-like precursors  
of different concentrations and different  
processing histories.

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

Gel concentration (%W/W)	Tm (°C.)	Crystallinity (%)
2	137	72
3	136.5	76
4	136.4	72
5	137	75
5*	129.8	73

\* Pseudo-gel preparation under isothermal and quiescent conditions.

The first column of Table I indicates the percent concentration of the gel-like precursor, the second column the melting temperature of the semicrystalline morphologies after the evaporation of the volatile solvent, and the third column the percent crystallinity of these semicrystalline morphologies. The melting endotherms were obtained at 5°C./min. under N<sub>2</sub>, and the degree of crystallinity was calculated, assuming that the heat of crystallization of a perfect polyethylene crystal is 293 J/g.

The thermal analysis results indicate that the melting temperature of the semicrystalline structures is independent of the concentration of the gel-like precursors which were obtained under non-isothermal non-quiescent conditions; however, it is lower when the gel-like precursor was prepared under isothermal and quiescent conditions. The higher melting endotherm of the crystalline structures at approximately 137°C. from pseudo-gels which were prepared

- 12 -

1 under non-isothermal or non-quiescent conditions indicates  
2 that the crystals should have an extended chain  
3 configuration and is in agreement with the optical  
4 observations (e.g., Fig. 4) that so-produced pseudo-gels are  
5 comprised to a large extent of a shish kebab fibrillar  
6 network.

7 The lower melting endotherm of the crystalline  
8 structure at 129.9°C. from a gel-like precursor which was  
9 prepared under isothermal and quiescent conditions (see  
10 Figs. 8 and 9) indicates that the crystals in this case have  
11 a chain-folded configuration, and, again, this is in  
12 agreement with the observation that the isothermally  
13 produced pseudo-gels under quiescent conditions are  
14 comprised of chain-folded crystals, like the stacks of  
15 single crystals and spherulites shown in Figs. 8 and 9.  
16 Also, it is clear from the data in Table I that the percent  
17 crystallinity of the semicrystalline structure is indepen-  
18 dent of the studied concentration range of its gel-like  
19 precursors as well as its processing history.

20 A semicrystalline UHMWPE structure which is prepared  
21 from a pseudo-gel intermediate combines morphological  
22 features which cannot be exhibited by the morphologies  
23 obtained either by compacting the as-received fine powder  
24 stock or by melt crystallization. These morphological  
25 features arise from (a) the controlled material cohesion  
26 which is incomplete in the compacted powders and the melt-  
27 crystallized morphologies prepared by partial fusion,  
28 (b) the diminished, vis à vis the excessive, "amount of  
29 physical entanglements" in the melt-crystallized morpholo-  
30 gies prepared by complete melting, and (c) the great  
31 variation of the crystalline morphology, from a chain-folded  
32 to an extended chain crystalline morphology, depending on  
33 the processing conditions during the preparation of the  
34 pseudo-gel precursor. The importance of the first two  
35 factors relates to the balanced enhancement of the deform-  
36 ability of the semicrystalline structures from gel-like  
37 precursors and their mechanical properties. The role of the  
38

- 13 -

1 third factor, and particularly the generation of a fibrillar  
2 network, comprised of extended-chain shish-kebab crystals,  
3 is important because such structure has a larger amount of  
4 free volume and consequently a high degree of porosity.

5 In comparison to the knitted and woven textures whose  
6 porosity can be adjusted to some extent by the thread size,  
7 interstices size, and the texturization of the synthetic  
8 fabric, the intrinsic fibrillar networks of this invention  
9 have the advantage that their porosity can be adjusted by  
10 thermal and mechanical means.

11 Thermal treatment may be brought about by heating the  
12 semicrystalline structure from a gel-like precursor to a  
13 temperature close to or above the melting point of the  
14 polymer and then cooling to ambient under modest compression  
15 (< approximately 50 Atm). This treatment resulted in a  
16 significant porosity reduction.

17 Similarly, when a semicrystalline structure from a  
18 gel-like precursor was compressed at ambient temperature  
19 under 500 Atm, its porosity was reduced as a result of the  
20 densification process that takes place during the  
21 compression process.

22 The porosity of the semicrystalline structure from a  
23 gel-like precursor may be controlled also by the evapora-  
24 tion rate of the volatile solvent during the drying process  
25 as well as by solid-state deformation. The effects of  
26 pressure, temperature, and solid-state deformation on the  
27 percent porosity of UHMWPE semicrystalline morphologies from  
28 gel-like precursors of different concentrations are  
29 summarized in Table II.

30

31

32

33

34

35

36

37

38

- 14 -

TABLE II

The effect of temperature, pressure and solid state deformation on the percent porosity of UHMWPE semicrystalline morphologies from gel-like precursors of different concentrations.

<u>UHMWPE Sample</u>	<u>Porosity (%)</u>
NIQ - pseudo-gel, 1%	90.5
NIQ - pseudo-gel, 2%	51
NIQ - pseudo-gel, 4%	63
SSD - pseudo-gel, 4%/DR = 4	49
NIQ - pseudo-gel, 5%	49
SSD - pseudo-gel, 5%/DR = 8	40
INQ - pseudo-gel, 5%	78
IQ - pseudo-gel, 5%	79.5
NIQ - pseudo-gel, 5%/compressed under 500 Atm	0.2
NIQ - pseudo-gel, 5%/heated to 140°C./50 Atm	8.7
NIQ - pseudo-gel, 8%	49
melt crystallized	7.3

NIQ = non-isothermal and quiescent conditions

INQ = isothermal and non-quiescent conditions

IQ = isothermal and quiescent conditions.

SSD = solid state deformed

DR = draw ratio

The porosity was calculated from density determination, assuming that the density of polyethylene is  $960 \text{ kgm}^{-3}$ . The symbol NIQ indicates that the gel-like precursor was prepared under non-isothermal and quiescent conditions; INQ indicates that the gel-like precursor was prepared under isothermal and non-quiescent conditions; and IQ indicates that the gel-like precursor was prepared under isothermal and quiescent conditions. SSD indicates a semicrystalline morphology from an NIQ-pseudo-gel which was

- 15 -

1 deformed in the solid state by tensile drawing at ambient  
2 temperature and at the indicated Draw Ratio (DR) determined  
3 by the cross-sectional areas before and after drawing.

4       The data in Table II indicates clearly that the  
5 porosity of the semicrystalline UHMWPE morphologies from  
6 gel-like precursors depends on the conditions of prepara-  
7 tion and can be adjusted over a wide range from 0 to 90% by  
8 a suitable choice of temperature and pressure, and solid-  
9 state deformation.

10       As shown in Fig. 2, UHMWPE pseudo-gel states contain-  
11 ing preferably a non-volatile solvent can be processed by  
12 molding or rolling under compression in step 31 to obtain  
13 thin gel-like film 32, preferably in a temperature range  
14 close to or above the temperature at which the pseudo-gel is  
15 formed (approximately 123°C.). Subsequently, the thin  
16 pseudo-gel film 32 can be wrapped in step 33 with or without  
17 tension on a mandrel to give a multilayer tubular structure,  
18 a process which allows also for the build up of the tubular  
19 wall thickness. Cohesion of the successive pseudo-gel layers  
20 is achieved by a molecular reptation process which may occur  
21 between adjacent layers and result in a tubular wall with  
22 fraying resistance.

23       The volatile solvent such as n-hexane replaced the  
24 non-volatile solvent in step 25 and is removed by evapora-  
25 tion in step 34, to give a moderately shrunk, hoop stressed  
26 structure 35, in a drying step. Typically, the evaporation  
27 of the volatile solvent from the pseudo-gel is accompanied  
28 by considerable shrinkage, which when constrained has the  
29 advantage of resulting in the development of hoop stresses  
30 which enhance (a) the molecular chain orientation in the  
31 circumferential direction and consequently the lateral  
32 strength of the tubular structures and (b) the molecular  
33 chain interpenetration in the overlapping pseudo-gel layers,  
34 thus resulting in a coherent tubular wall.

35       Further enhancement of the mechanical performance of  
36 the tubular structures can be achieved by solid-state  
37 drawing in step 36 of the hoop-stressed dried tube 35. The  
38

- 16 -

1 process may result in tubular products 37 having a biaxially  
2 oriented fibrillar network structure with mechanical  
3 integrity along and across the draw direction. This  
4 integrity results from the superposition of the circumferen-  
5 tial orientation, which is obtained by the constrained  
6 shrinkage during the evaporation of the volatile solvent,  
7 and the axial orientation during the solid-state deformation  
8 process on the mandrel. The solid-state deformation was  
9 performed at ambient temperature, and the draw ratio (DR)  
10 was calculated from the displacement of markers on the  
11 tubular wall after drawing.

12 Fig. 10 shows in a solid line curve average experi-  
13 mental modulus values at different draw ratios. The  
14 variation of experimentally determined initial modulus with  
15 the draw ratio is non-linear for the solid-state-drawn  
16 UHMWPE semicrystalline morphologies of this invention to a  
17 draw ratio of 8, in contrast to the previously established  
18 linear relation for melt-crystallized, high-density (not  
19 ultra-high molecular weight) polyethylene resins shown in  
20 Fig. 11; the difference is presumably due to the high  
21 porosity of the UHMWPE semicrystalline morphologies, in  
22 comparison to the low-porosity, melt-crystallized, high-  
23 density polyethylenes, which diminishes and allows for  
24 effective load transmission at significantly higher draw-  
25 ratios. Fig. 10 shows in a broken-line curve a graph of  
26 experimentally determined maximum initial modulus values  
27 from my new material at different draw ratios.

28 Fig. 3 shows a process much like that of Fig. 2.  
29 Pieces of pseudo-gel 40 are compressed at step 41 to make a  
30 gel-like sheet 42. The sheet 42 is wrapped around a mandrel  
31 43 to produce a gel-like tube 44, which is then extracted  
32 at 45 to give a dry tube 46. This may be further processed,  
33 as at 47, as by drawing, or may be received from the mandrel  
34 43 to give a vascular product 48.

35 Alternative methods for the preparation of tubular  
36 products with a biaxially oriented fibrillar network  
37 structure include processes such as solid-state extrusion  
38

- 17 -

1 through inverted conical dies and blowing air through the  
2 tubes. Both processes are also suitable for the preparation  
3 of biaxially oriented UHMWPE films which can be obtained by  
4 splitting the biaxially oriented tubes along their length.  
5 Also, some or most of the conventional thermoplastic  
6 processes, such as rolling, extrusion, drawing, compression  
7 molding, forging, and extrudo-rolling are amenable to  
8 processing UHMWPE semicrystalline morphologies from gel-like  
9 precursors into products with different profiles and  
10 geometric configurations and with adjustable mechanical  
11 properties over a wide range.

12 Tests in vivo indicate that artificial vascular  
13 prostheses made by this process can be handled conveniently  
14 and sutured to the natural vascular system readily. The  
15 vascular prostheses, isotropic UHMWPE semicrystalline tubes  
16 approximately 5 - 6 cm. long were implanted in the iliac  
17 aorta of mature dogs for an observation period of up to four  
18 months and exhibited very satisfactory anastomosis. Bleeding  
19 through the wall of the prosthesis was not observed during  
20 the implantation process. The prostheses are uniformly  
21 expansive under the pulsatile blood pressure and are  
22 flexible so that they bend without sharp corners. They do  
23 not show aneurysms at and beyond the anastomotic interfaces  
24 or along their body. (Aneurysms are local and progressive  
25 enlargements of vessel because of loss of vascular  
26 elasticity.)

27 The vascular prostheses of this invention can be  
28 fabricated in different geometric configurations, straight,  
29 crimped, smooth, or rough wall surfaces with adjustable  
30 porosities and mechanical properties over a wide range.  
31 Furthermore, this invention includes within its scope the  
32 use of isotropic and anisotropic UHMWPE morphologies from  
33 gel-like precursors in other biomedical application, such  
34 as orthopedic prostheses, sutures, and ligatures, in which  
35 a suitable combination of porosity and mechanical properties  
36 is necessary.

37

38

- 18 -

1        Other polymers which fall in the same category and  
2 can be obtained from gel-like precursors are ultra-high-  
3 molecular-weight polypropylene, polyvinyl alcohol, and  
4 nylons (polyamides).

5        To those skilled in the art to which this invention  
6 relates, many changes in construction and widely differing  
7 embodiments and applications of the invention will suggest  
8 themselves without departing from the spirit and scope of  
9 the invention. Such embodiments may include the fabrication  
10 of UHMWPE knitted and woven vascular prostheses, sutures,  
11 and composite structures of UHMWPE filamentary and non-  
12 filamentary semicrystalline morphologies. The disclosures  
13 and the descriptions herein are purely illustrative and are  
14 not intended to be in any sense limiting.

15        What is claimed is:

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

- 19 -

1        1. A pseudo-gel comprising a suitable solvent in an  
2 amount of 1 to 10 percent by weight and an ultra-high-  
3 molecular-weight polyethylene in an amount of 99 to 90  
4 percent by weight, said polyethylene being a semicrystalline  
5 network with adjustable crystalline morphology comprising  
6 randomly dispersed and oriented chain-folded single  
7 crystals, stacks of single crystals, spherulite crystals,  
8 and extended-chain shish-kebab-type of fibrils with lengths  
9 up to a few millimeters and widths up to 20  $\mu\text{m}$ .

10

11        2. The semicrystalline ultra-high molecular-weight  
12 polyethylene obtained by removal of said solvent from the  
13 pseudo-gel of claim 1.

14

15        3. A semicrystalline morphology of ultra-high-  
16 molecular-weight polyethylene comprising randomly dispersed  
17 and oriented single crystals, stacks of single crystals,  
18 spherulitic crystals, and shish-kebab-type of fibrils with  
19 lengths up to a few millimeters and widths up to 20  $\mu\text{m}$ ., a  
20 melting point of 125 - 140°C., measured at a heating rate of  
21 5°C./min., a crystallinity of about 70%, measured on the  
22 basis that the heat of fusion of a perfect polyethylene  
23 crystal is 293 J/g., and a porosity from about 50 to 90%,  
24 measured on the basis that the density of polyethylene is  
25 960 Kg/m<sup>3</sup>.

26

27        4. A method for making an ultra-high-molecular-weight  
28 polyethylene product for use in vascular prostheses and the  
29 like, comprising,

30        dissolving ultra-high-molecular-weight polyethylene in  
31 a solvent at an elevated temperature,

32        cooling the solution to temperature at which polymer  
33 crystals grow into an intercrystalline network that produces  
34 a pseudo-gel state, and

35        extracting the solvent to produce a semi-crystalline  
36 porous morphology.

37

38

- 20 -

1       5. The method of claim 4 wherein the cooling step is  
2 done under non-isothermal, quiescent conditions.  
3

4       6. The method of claim 5 followed by drawing the  
5 semicrystalline morphology resulting from the extracting  
6 step, at a draw ratio of at least 5 and at a temperature in  
7 the range from ambient temperature to a temperature not  
8 exceeding the melting point of said semicrystalline  
9 morphology.

10

11       7. The method of claim 5, comprising, between the  
12 cooling and extracting steps, the step of compressing the  
13 gel.  
14

15       8. The method of claim 4 wherein the cooling step is  
16 done under isothermal, non-quiescent conditions.  
17

18       9. The method of claim 4 wherein the cooling step is  
19 done under isothermal, quiescent conditions.  
20

21       10. A method for making an ultra-high-molecular-weight  
22 polyethylene product for use in vascular prostheses and the  
23 like, comprising,  
24           dissolving ultra-high-molecular-weight polyethylene in  
25 a non-volatile solvent at an elevated temperature,  
26           cooling the solution to a temperature at which polymer  
27 crystals grow into an intercrystalline network that produces  
28 a pseudo-gel state, and  
29           extracting the non-volatile solvent to produce a semi-

30 crystalline porous morphology.  
31

32       11. The method of claim 10 wherein the cooling step is  
33 done under non-isothermal, quiescent conditions.  
34

35

36

37

38

- 21 -

1        12. The method of claim 11 followed by drawing the  
2 resulting product at a temperature no lower than ambient and  
3 no higher than the melting point of the semicrystalline  
4 porous morphology and at a draw ratio of at least 5.  
5

6        13. The method of claim 11, comprising, between the  
7 cooling and extracting steps, compressing the gel between  
8 plates at 100° to 160°C.  
9

10        14. The method of claim 10 wherein the cooling step is  
11 done under isothermal, non-quiescent conditions.  
12

13        15. The method of claim 10 wherein the cooling step is  
14 done under isothermal, quiescent conditions.  
15

16        16. A method for making a tubular profile of ultra-  
17 high-molecular-weight polyethylene with adjustable wall  
18 thickness, comprising the successive steps of  
19              wrapping an ultra-high-molecular-weight polyethylene  
20 pseudo-gel containing nonvolatile solvent on a mandrel,  
21              extracting the solvent from the pseudo-gel with a more  
22 volatile solvent, and  
23              evaporating the volatile solvent from the tubular  
24 profile.  
25

26        17. The method of claim 16, comprising making an  
27 anisotropic ultra-high-molecular-weight polyethylene tubular  
28 structure by following the evaporating steps with the step  
29 of stretching the tube on the mandrel.  
30

31        18. The method of claim 17 in which the temperature of  
32 stretching is from ambient temperature to the melting point  
33 of the semi-crystalline porous morphology obtained after the  
34 evaporating step.  
35

36        19. The method of claim 17 in which the draw ratio is  
37 at least 5x.  
38

- 22 -

1        20. A method for making a tubular profile of ultra-  
2 high-molecular-weight polyethylene with adjustable wall  
3 thickness, comprising the steps of:

4              dissolving said ultra-high-molecular-weight poly-  
5 ethylene in non-volatile solvent at an elevated temperature,  
6              cooling the solution to temperature at which polymer  
7 crystals grow into an intercrystalline network that provides  
8 a pseudo-gel,

9              wrapping the gel around a mandrel,  
10             extracting the non-volatile solvent from the gel with  
11 a volatile solvent, and  
12             evaporating the volatile solvent from the tubular  
13 profile.

14

15        21. The method of claim 20 followed by stretching the  
16 tube on the mandrel at a temperature from ambient to 135°C.  
17 and at a draw ratio of at least 5x.

18

19        22. A tube of ultra-high-molecular-weight polyethylene  
20 semicrystalline morphology useful for vascular prostheses  
21 and having a Young's modulus of at least 3 GPa obtained by  
22 wrapping an ultra-high-molecular-weight polyethylene pseudo-  
23 gel on a mandrel, extracting the solvent with more volatile  
24 solvent and evaporating volatile solvent.

25

26        23. The tube of claim 22 in which the porosity is  
27 adjustable over the range of 0.2% to 90%.

28

29        24. A pseudo-gel comprising a suitable solvent in an  
30 amount of 1 to 10 percent by weight and an ultra-high-  
31 molecular-weight polymer in an amount of 99 to 90 percent by  
32 weight, said polymer being a semicrystalline network with  
33 adjustable crystalline morphology comprising randomly  
34 dispersed and oriented chain-folded single crystals, stacks  
35 of single crystals, spherulite crystals, and extended-chain  
36 shish-kebab-type of fibrils with lengths up to a few  
37 millimeters and widths up to 20 µm.

38

- 23 -

1        25. The semicrystalline ultra-high molecular-weight  
2 polymer obtained by removal of said solvent from the pseudo-  
3 gel of claim 24.  
4

5        26. A semicrystalline morphology of ultra-high-  
6 molecular-weight polymer comprising randomly dispersed and  
7 oriented single crystals, stacks of single crystals,  
8 spherulitic crystals, and shish-kebab-type of fibrils with  
9 lengths up to a few millimeters and widths up to 20  $\mu\text{m}$ ., a  
10 melting point of 125 - 140°C., measured at a heating rate of  
11 5°C./min., a crystallinity of about 70%, and a porosity  
12 from about 50 to 90%.

13

14        27. A method for making an ultra-high-molecular-weight  
15 polymer product for use in vascular prostheses and the like,  
16 comprising,

17            dissolving ultra-high-molecular-weight polymer in a  
18 solvent at an elevated temperature,

19            cooling the solution to temperature at which polymer  
20 crystals grow into an intercrystalline network that produces  
21 a pseudo-gel state, and

22            extracting the solvent to produce a semi-crystalline  
23 porous morphology.

24

25        28. The method of claim 27 wherein the cooling step is  
26 done under non-isothermal, quiescent conditions.

27

28        29. The method of claim 28 followed by drawing the  
29 semicrystalline morphology resulting from the extracting  
30 step, at a draw ratio of at least 5 and at a temperature in  
31 the range from ambient temperature to a temperature not  
32 exceeding the melting point of said semicrystalline  
33 morphology.

34

35        30. The method of claim 28, comprising, between the  
36 cooling and extracting steps, the step of compressing the  
37 gel.

38

- 24 -

1        31. The method of claim 27 wherein the cooling step is  
2 done under isothermal, non-quiescent conditions.  
3

4        32. The method of claim 27 wherein the cooling step is  
5 done under isothermal, quiescent conditions.  
6

7        33. A method for making a tubular profile of ultra-  
8 high-molecular-weight polymer with adjustable wall  
9 thickness, comprising the successive steps of  
10      wrapping an ultra-high-molecular-weight polymer  
11 pseudo-gel containing nonvolatile solvent on a mandrel,  
12      extracting the solvent from the pseudo-gel with a more  
13 volatile solvent, and  
14      evaporating the volatile solvent from the tubular  
15 profile.  
16

17       34. The method of claim 33, comprising making an  
18 anisotropic ultra-high-molecular-weight polyethylene tubular  
19 structure by following the evaporating steps with the step  
20 of stretching the tube on the mandrel.  
21

22       35. The method of claim 34 in which the temperature of  
23 stretching is from ambient temperature to the melting point  
24 of the semi-crystalline porous morphology obtained after the  
25 evaporating step.  
26

27       36. The method of claim 34 in which the draw ratio is  
28 at least 5x.  
29

30       37. A method for making a tubular profile of ultra-  
31 high-molecular-weight polyethylene with adjustable wall  
32 thickness, comprising the steps of:  
33      dissolving said ultra-high-molecular-weight poly-  
34 ethylene in non-volatile solvent at an elevated temperature,  
35      cooling the solution to a temperature at which polymer  
36 crystals grow into an intercrystalline network that provides  
37 a pseudo-gel,  
38

- 25 -

1       wrapping the gel around a mandrel,  
2       extracting the non-volatile solvent from the gel with  
3       a volatile solvent, and  
4       evaporating the volatile solvent from the tubular  
5       profile.

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

1 / 6

FIG. 1

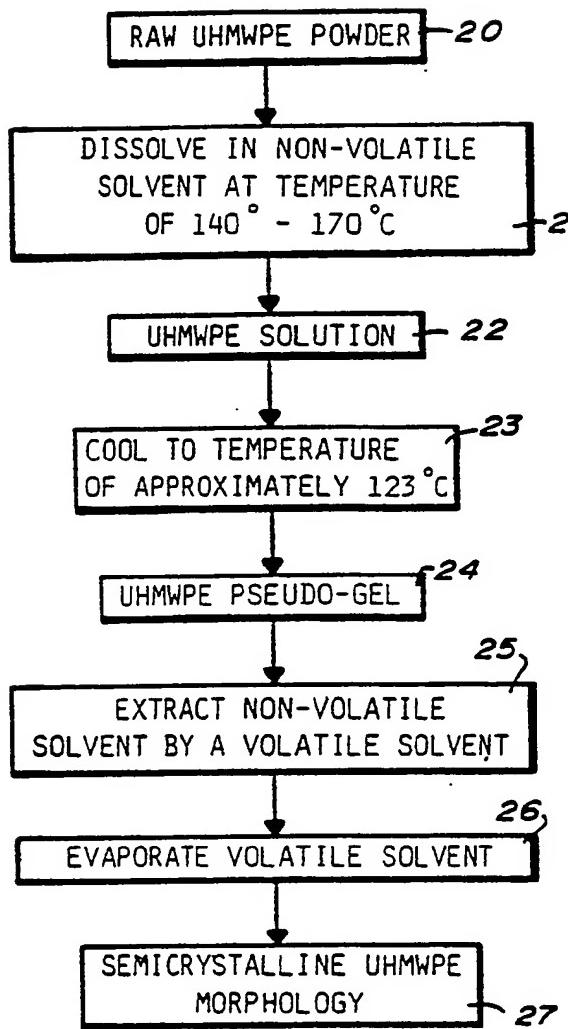
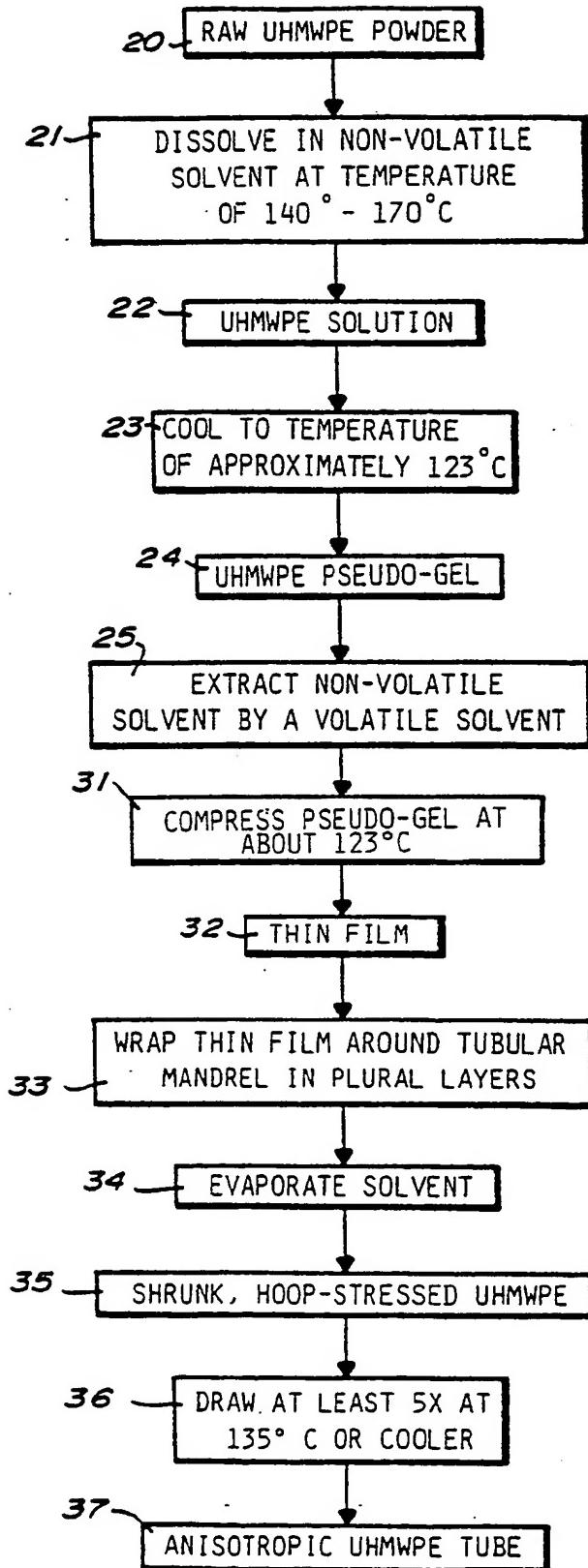
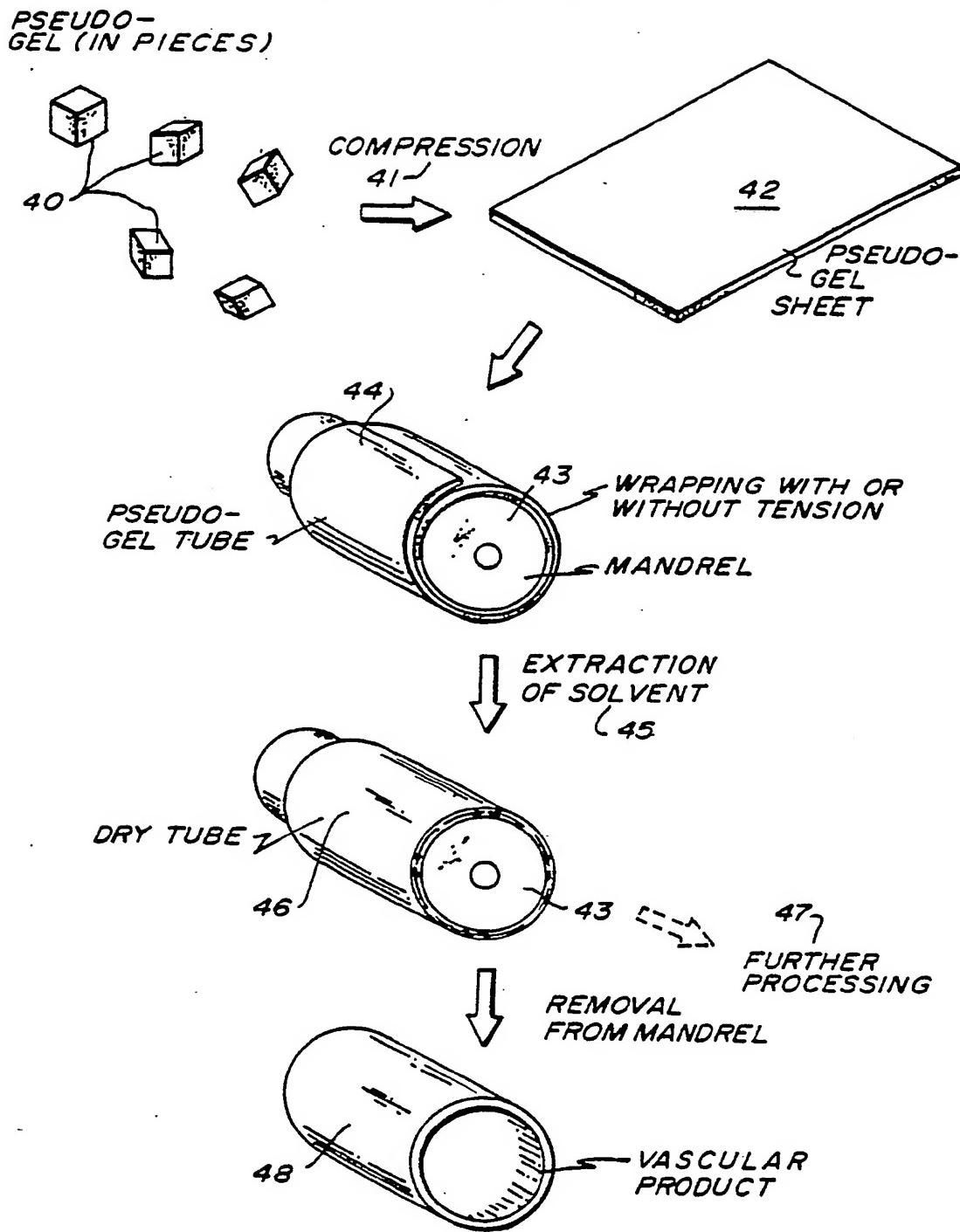


FIG. 2



2 / 6

FIG. 3



3 / 6



FIG. 4



FIG. 7

4 / 6

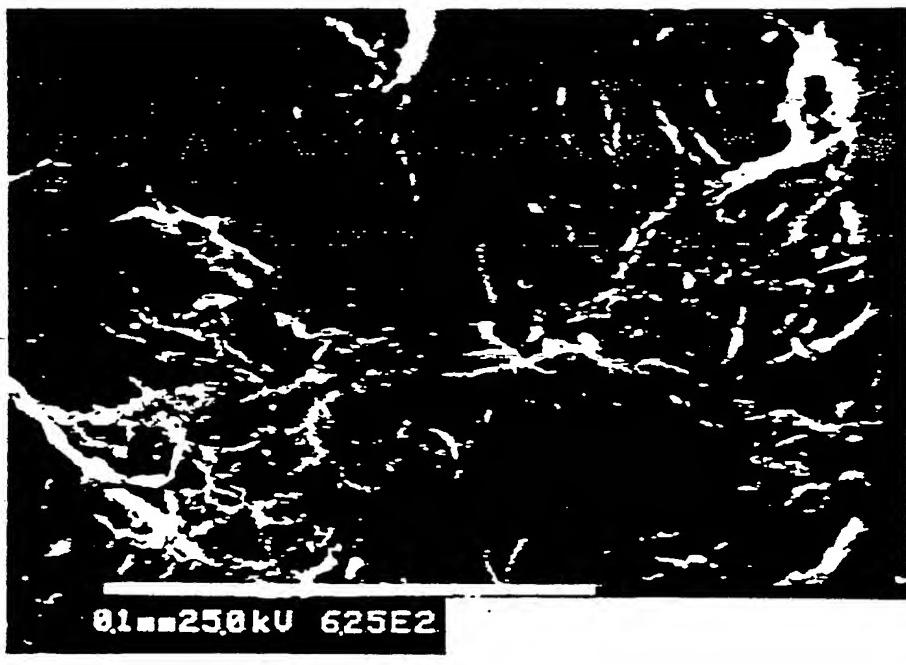


FIG. 5



FIG. 6

5 / 6



FIG. 8

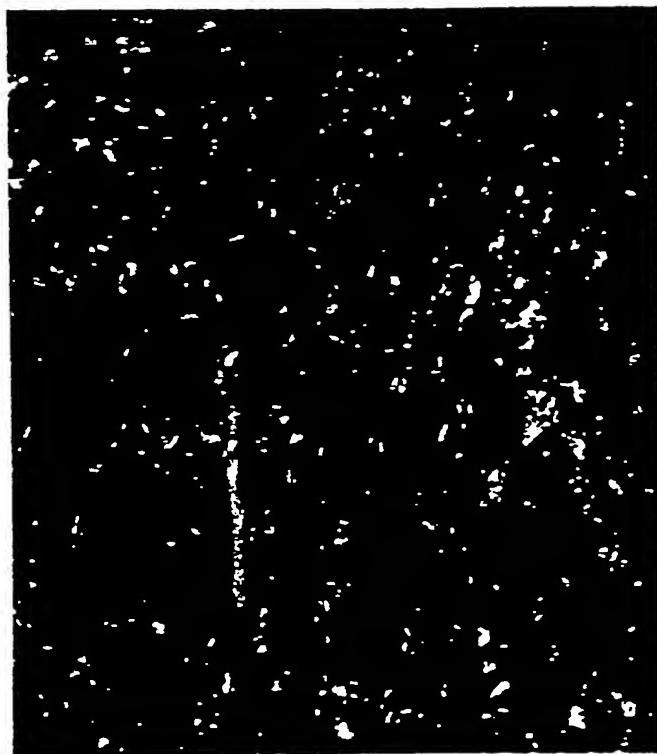


FIG. 9

6 / 6

FIG. 11

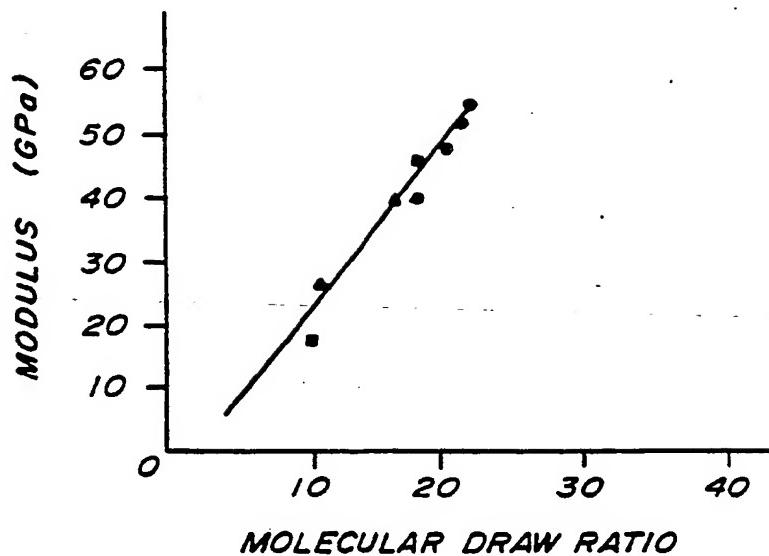
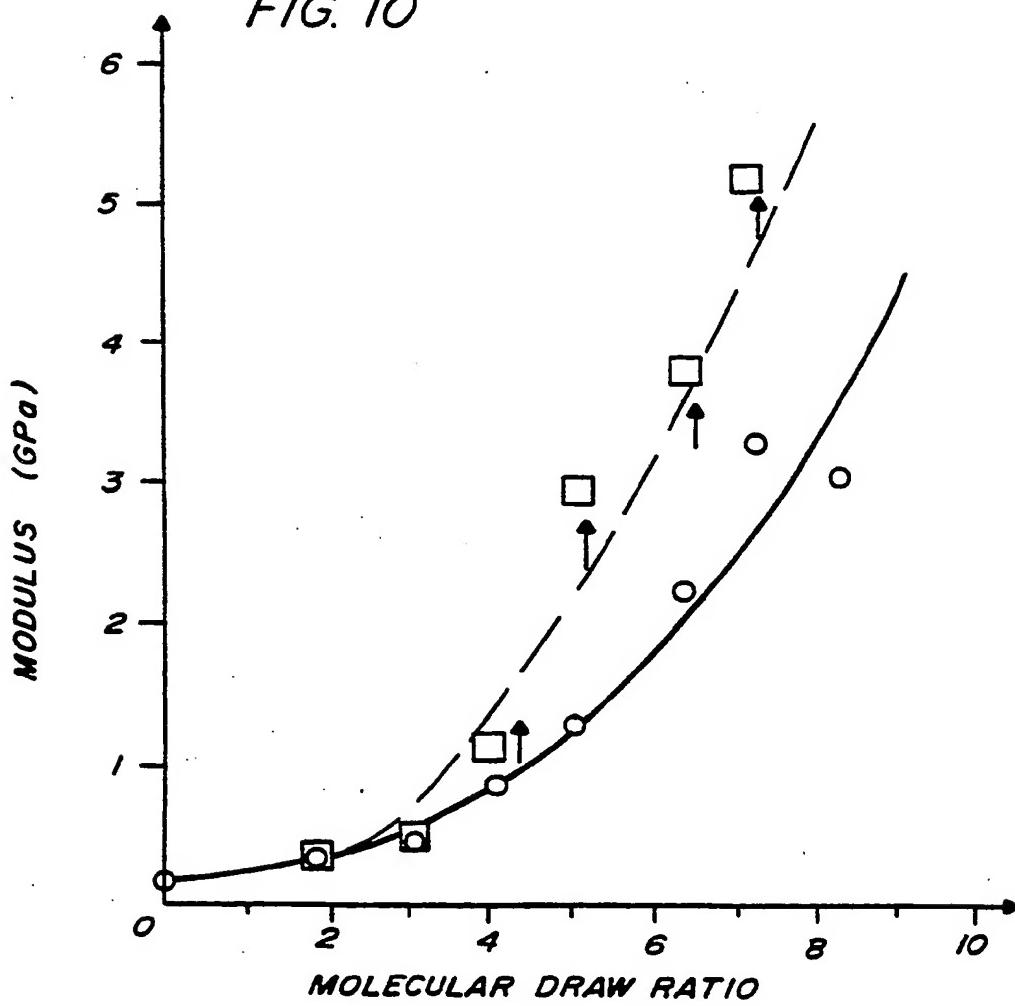


FIG. 10



# INTERNATIONAL SEARCH REPORT

International Application No PCT/US85/02078

## 1. CLASSIFICATION & SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>3</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

**IPC4 C08J 9/28**

## II. FIELDS SEARCHED

### Minimum Documentation Searched <sup>4</sup>

Classification System	Classification Symbols
U.S.	428/401 402; 526/352; 264/41, 49; 521/79, 143 524/585

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>14</sup>

Category <sup>6</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
A	US, A, 3,954,927 PUBLISHED 04 MAY 1976 DULING ET AL	1-37
A	US, A, 3,984,387 PUBLISHED 05 OCTOBER 1976 LIU ET AL	1-37
A	US, A, 3,997,648 PUBLISHED 14 DECEMBER 1976 DAVIS ET AL	1-37
A	US, A, 4,020,266 PUBLISHED 26 APRIL 1977 FRANK ET AL	1-37
A	US, A, 4,246,390 PUBLISHED 20 JANUARY 1981 SEAVEN	1-37
A	US, A, 4,413,110 PUBLISHED 01 NOVEMBER 1983 KAVESH ET AL	1-37

\* Special categories of cited documents: <sup>15</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

## IV. CERTIFICATE

Date of the Actual Completion of the International Search <sup>19</sup>

06 JANUARY 1986

Date of Mailing of this International Search Report <sup>20</sup>

24 JAN 1986

International Searching Authority <sup>21</sup>

ISA/US

Signature of Authorized Officer <sup>22</sup>

P.R. Michl